JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 10, October 2008, p. 2771 - 2776

Spectral analysis of Pr^{3+} & Tm^{3+} ions doped fluoro- phospho - borate glasses

B. SUDHAKAR REDDY[a*], S. BUDDHUDU[b], S. R. K. RAO[c], P. NARESH BABU[c]
[a]*Department of Physics, Sri Venkateswara Degree College ,Kadapa-516003, India*
[b]*Department of Physics, Sri Venkateswara University, Tirupati-517502, India*
[c]*Department of Physics, Indian Institute of Science, Bangalore - 560 012, India*

Optical analysis of (0.2mol %) Pr^{3+}&Tm^{3+} ions doped fluoro-phospho-borate glasses have been reported in the following glass compositions: 69.8 B_2O_3 – 10 P_2O_5 – 10(ZnO/CdO/TeO_2) – 10 AlF_3 /10LiF Measured absorption spectra of Pr^{3+}: fluoro-phospho-borate glasses have shown eight absorption bands at 443, 469, 481, 589 , 1008, 1419, 1523 and 1930 nm which correspond to the transitions $^3H_4 \rightarrow {}^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$, $^1G_4$, $^3F_4$, $^3F_3$ and $^3F_2$ respectively. Absorption spectra of Tm^{3+}: glasses have revealed five absorption bands at 466, 685, 790, 1206 and 1644 nm which belong to the transitions $^3H_6 \rightarrow {}^1G_4$, $^3F_3$, $^3H_4$, $^3H_5$ and $^3F_4$ respectively. Pr^{3+}: glasses, with an excitation at 442nm ($^3H_4 \rightarrow {}^3P_2$), a *orange-red* emission at 600 nm ($^1D_2 \rightarrow {}^3H_4$) has been observed. In the case of Tm^{3+}: glasses, upon excitation with 355nm ($^3H_6 \rightarrow {}^1D_2$), blue emissions at 452 nm ($^1D_2 \rightarrow {}^3F_4$) and at 476 nm ($^1G_4 \rightarrow {}^3H_6$) are observed. From the measured NIR emission spectra of Pr^{3+}: fluoro-phospho-borate glasses, an NIR emission at 1354nm ($^1G_4 \rightarrow {}^3H_5$) and form Tm^{3+}: glasses, an NIR emission ($^3F_4 \rightarrow {}^3H_6$) at 1809 nm are observed with an Ar^+ laser (514.5 nm) as the excitation source.

(Received August 2, 2008; accepted August 14, 2008)

Keywords: Pr^{3+} and Tm^{3+}, Glasses, Spectral analysis, B_2O_3 – P_2O_3 – ZnO CdO TeO_2-AlF_3 glasses

1. Introduction

Glasses are attractive materials for different applications, based on their physical, electrical and optical properties [1-15]. Optical systems based on phosphates and fluorides have been identified as good glassy materials due to their good glass forming ability, hardness, transparency and resistance towards the moisture and with an extended IR transmission ability. Several systems with B_2O_3 have been studied because they are interesting non linear optical materials [16-21]. In order to improve the glass quality and its optical performance from the fluoro-phospho-borate glasses, oxides such ZnO, CdO and TeO_2 have been added separately along side two other property improving network modifiers (NWM) namely LiF/AlF_3. Rare earth ions are incorporated into these boro-fluoro-phosphate glasses in order to characterize their optical properties. From the literature, it has been noticed that Pr^{3+} and Tm^{3+} doped glassy materials have attracted a great deal of attention due to their applications in optical communication [22-38]. Thulium glasses have also been of great importance due to their uses as lasers and fiber optic amplifiers [39 - 46]. We have recently reported on the physical properties and XRD, FT-IR, DTA features of boro-fluoro-phosphate reference glasses [45] we have recently analyzed the spectral properties of Eu^{3+}&Tb^{3+} ions doped in borophosphate oxyfluoride glasses [46]. In the present work, we report on the spectral properties of Pr^{3+} and Tm^{3+} ions doped fluoro-phospho-borate glasses.

2. Experimental procedure

2.1 Glasses Preparation

Two new series of (0.2mol %) Pr^{3+} & Tm^{3+}ions doped fluoro-phospho –borate optical glasses systems have been prepared by adopting the quenching technique and their chemical compositions (mol%) are given below:

Series A : 69.8 B_2O_3 – 10 P_2O_5 – 10(ZnO/CdO/TeO_2) – 10 AlF_3

Series B: 69.8 B_2O_3 – 10 P_2O_5 – 10(ZnO/CdO/TeO_2) – 10 LiF

The chemicals used in the present work were reagent grade of H_3BO_3, $(NaPO_3)_6$, Pr_2O_3, Tm_2O_3, ZnO, CdO, AlF_3 and LiF. Appropriate amounts of chemicals were weighed and powdered finely, in an agate mortar. Each batch was weighing about 10 g, those were melt at 950^0C in an electrical furnace for an hour. These melts were quenched in between two brass plates for obtaining 2-3cm diameter glass discs with 0.3cm in thickness. Glasses thus obtained were annealed at 200^0C for an hour to remove thermal strains.

2.2 Measurements

The Vis-NIR absorption spectra of Pr^{3+} &Tm^{3+} : fluoro-phospho-borate glasses were measured on a Varian-Cary-Win Spectrometer (JASCO V-570) . Both the excitation and visible emission spectra of Pr^{3+} and Tm^{3+} glasses were measured on a SPEX Fluorolog -2

Fluorimeter (Model II) with a Datamax software to acquire the data with a Xe-arc lamp (150W) as the excitation source.

NIR photoluminescence spectra of the Pr^{3+} &Tm^{3+}: glasses were also measured on a Horiba Triax-550 grating monochromator (JOBIN YVONHORIBA) equipped with a liquid nitrogen cooled InGaAs photo detector (Electro-Optical System –Inc) in the wavelength range of 800-2400 nm and a lock-in-amplifier (SR 830 DSP, Standard Research Systems) with an Ar^{+} laser (514.5nm) (LEXEL MODEL 85 ION LASER, 5mW-200mW) as the excitation source.

3. Results and discussions

3.1. Pr^{3+}:Fluoro-phospho-borate glasses

All the glasses have revealed amorphous nature (Figs. 1a&1b).

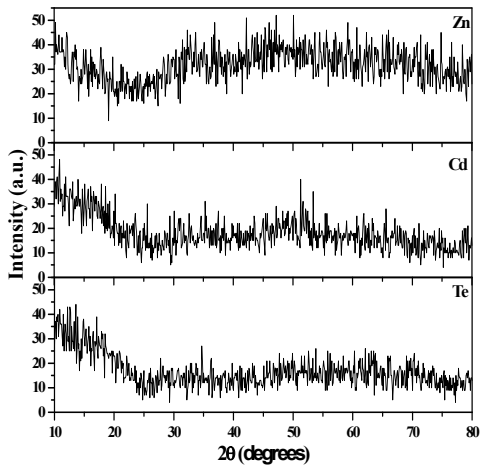

Fig.1a. XRD profile of Pr^{3+}: Fluoro-phospho- borate glasses (Series-A)

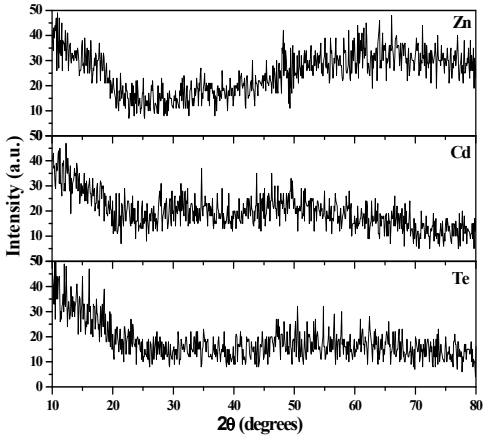

Fig.1b. XRD profile of Pr^{3+}: Fluoro-phospho- borate glasses (Series-B).

Vis-NIR optical absorption spectra of Pr^{3+}: fluoro-phospho-borate in the spectral range (400-2200nm) are shown in Figs. 2a&2b, for a comparison.

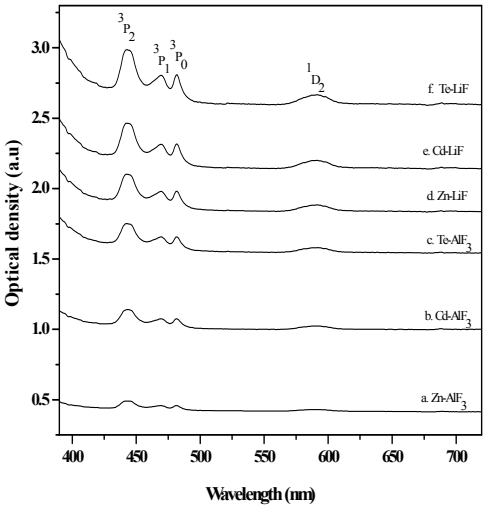

Fig. 2a. Visible absorption spectra of Pr^{3+}: Fluoro-phospho-borate glasses

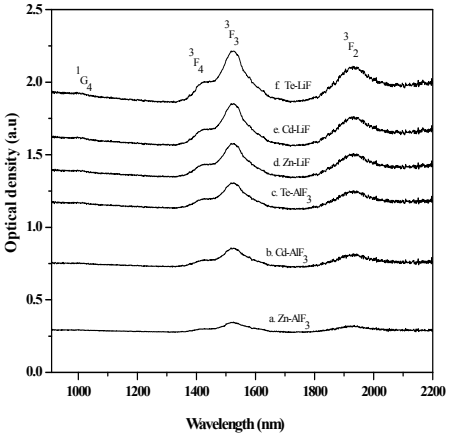

Fig.2b. NIR absorption spectra of Pr^{3+}: Fluoro-phospho- borate glasses

All samples have revealed eight absorption bands at 1930 nm ($^3H_4 \rightarrow {}^3F_2$), 1523 nm ($^3H_4 \rightarrow {}^3F_3$), 1419 nm ($^3H_4 \rightarrow {}^3F_4$), 1008nm ($^3H_4 \rightarrow {}^1G_4$), 589 nm ($^3H_4 \rightarrow {}^1D_2$), 481 nm ($^3H_4 \rightarrow {}^3P_0$), 469nm ($^3H_4 \rightarrow {}^3P_1$) and 443 nm ($^3H_4 \rightarrow {}^3P_2$). Bands have been assigned to electronic transitions based on the earlier reports on Pr^{3+} ion in other optical systems [47, 48]. It is clear from the Figs.1a&1b that, the overall appearance of the spectra of Pr^{3+} ion in (both the series of A & B) in all six glasses are similar from one to another but the band relative intensities are changing.

The excitation spectrum of Pr^{3+}: lithium-tellurium glass (Fig.3) shows two excitation bands ($^3H_4 \rightarrow {}^3P_{2,0}$) at 442 and 466nm respectively and emission spectra (Fig.4) of Pr^{3+}: glasses show that the emission ($^1D_2 \rightarrow {}^3H_4$) at 600 nm shows a orange-red emission.

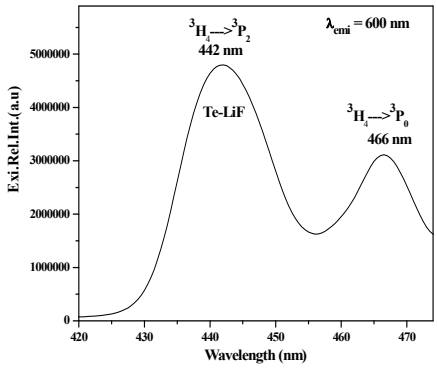

Fig.3. Excitation spectra of Pr^{3+}: Boro-fluoro- phosphate glasses

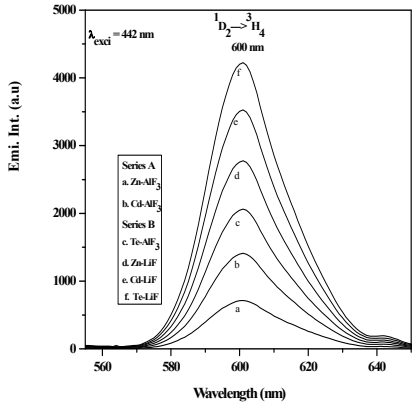

Fig. 4. Visible emission spectrum of Pr^{3+}: Fluoro-phospho-borate glasses.

Fig.5 presents the decay curves of the orange-red emission ($^1D_2 \rightarrow {}^3H_4$) at 600 nm of Pr^{3+}: glasses along with their lifetimes, upon excitation at 442nm ($^3H_4 \rightarrow {}^3P_2$).

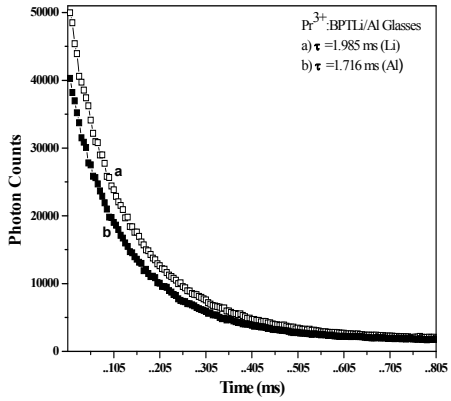

Fig. 5. Decay curves of the orange-red emission transition (600 nm) of Pr^{3+}: Fluoro – phosphor - borate glasses with excitation at 442nm

Fig.6 shows the NIR emission spectra of Pr^{3+}: fluoro-phospho-borate (both the series of A & B) with an NIR emission ($^1G_4 \rightarrow {}^3H_5$) at 1355nm upon excitation with an Ar^+ laser (514.5 nm). The shapes and widths are similar to those observed earlier for the1355nm emission of Pr^{3+}in other fluoride glasses like ZBLAN [49] and AlF_3 - fluoride glasses [50], fluorogallate and fluoro-gallo-indate glasses [51].

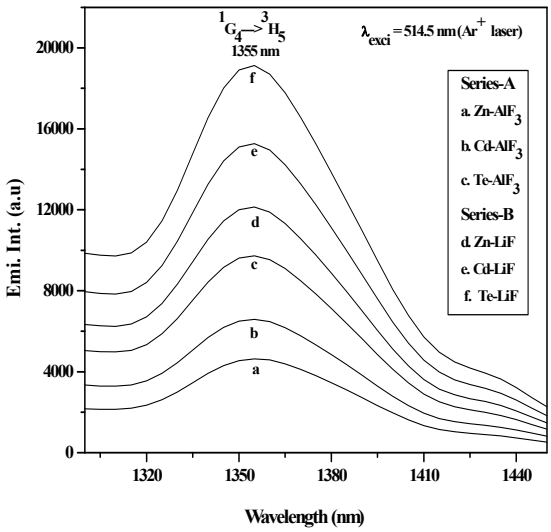

Fig. 6. NIR Emission spectra of Pr^{3+}: Fluoro-phospho-borate glasses

3.2 Tm^{3+}: Fluoro-phospho-borate glasses

The Vis-NIR optical absorption spectra of Tm^{3+}: fluoro-phospho-borate in the spectral range (400-1800nm) are shown in Figs. 7a & 7b for a comparison.

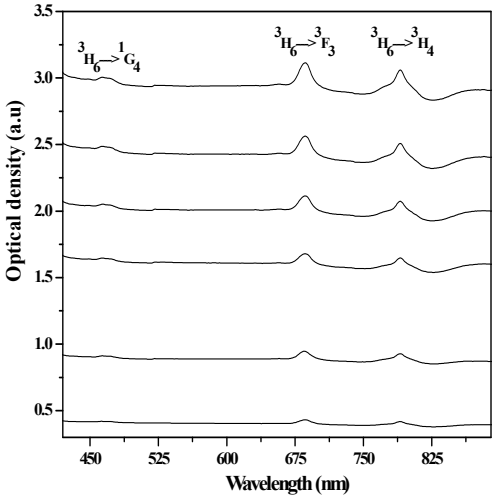

Fig.7a. Visible absorption spectra of Tm^{3+}: Fluoro-phospho-borate glasses.

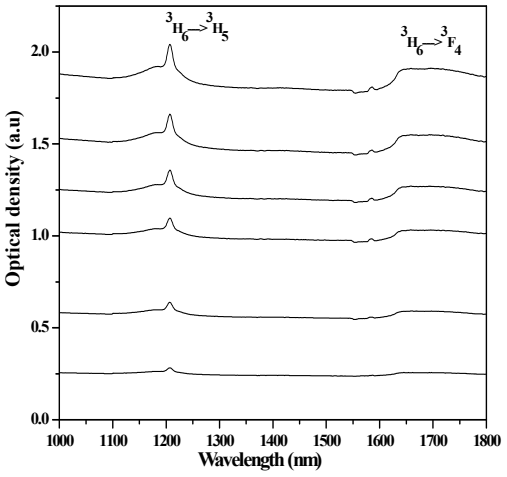

Fig.7b. NIR absorption spectra ofTm^{3+}: Fluoro-phospho-borate glasses

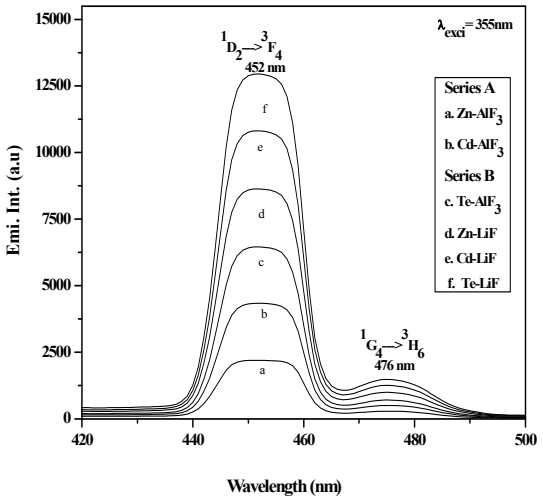

Fig.9: Visible emission spectra of Tm^{3+}: Fluoro-phospho-borate glasses

All samples have revealed five absorption bands at 1644nm ($^3H_6 \rightarrow {}^3F_4$), 1206nm ($^3H_6 \rightarrow {}^3H_5$), 790 nm ($^3H_6 \rightarrow {}^3H_4$), 685nm ($^3H_6 \rightarrow {}^3F_3$) and 466 nm ($^3H_6 \rightarrow {}^1G_4$). Assignments to these bands have been made by following the previously reported results on Tm^{3+} ion in other systems [52-54].

The excitation spectrum of Tm^{3+}: lithium-tellurium glasses (Fig.8) shows an excitation band ($^3H_6 \rightarrow {}^1D_2$) at 355nm,with which emission spectra of Tm^{3+}: fluoro-phospho-borate (Fig.9) are measured and from which two emission bands ($^1D_2 \rightarrow {}^3F_4$) at 452nm and ($^1G_4 \rightarrow {}^3H_6$) at 466nm are observed.

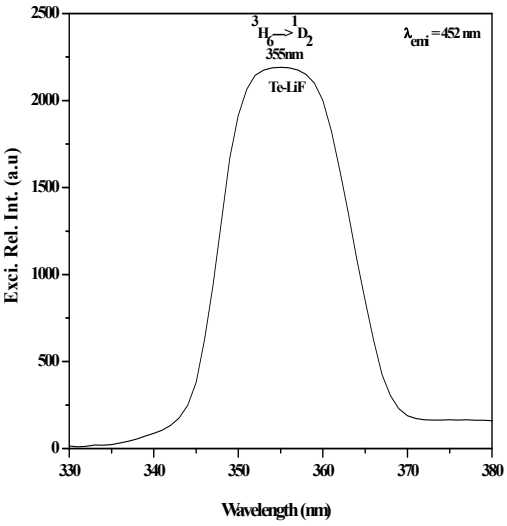

Fig.8: Excitation spectrum of Tm^{3+}: Fluoro-phospho- borate glasses

Fig.10 presents the decay curves of the blue emission ($^1D_2 \rightarrow {}^3F_4$) at 452nm of Tm^{3+}: fluoro-phospho-borate (Li orAl) with excitation at 355nm ($^3H_6 \rightarrow {}^1D_2$) .

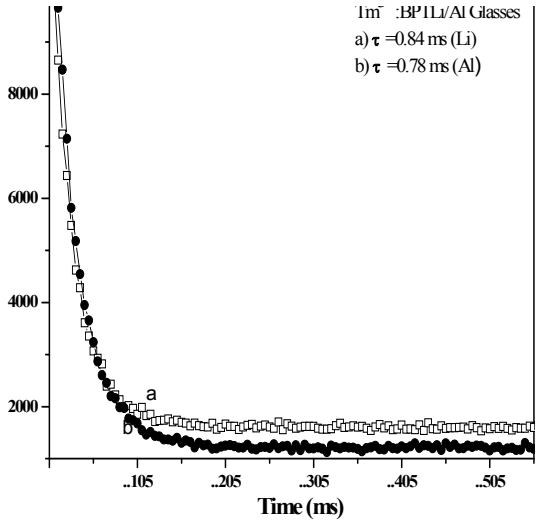

Fig.10. Decay curves of the blue emission transition of (452nm) of Tm^{3+}: Fluoro-phospho- borate glasses with excitation at 355 nm

Fig. 11. shows the NIR emission spectra of Tm^{3+}: fluoro-phospho-borate (both the series of glasses) with an emission band ($^3F_4 \rightarrow {}^3H_6$) at 1809 nm upon excitation with an Ar^+ laser (514.5 nm). The shapes and widths are similar to those observed for the 1809 nm emission of Tm^{3+}in other oxyfluoride glass ceramics [55], lead fluoride-tellurite glasses [52] and lead niobium germanate glasses [56].

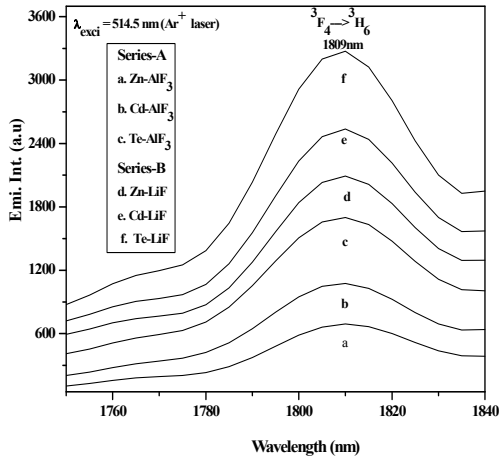

Fig.11. NIR Emission spectra of Tm^{3+}: Fluoro-phospho-borate glasses.

4. Conclusions

In summary, it could be concluded that we have successfully developed highly transparent, moisture resistant and more stable Pr^{3+} &Tm^{3+}ions doped fluoro-phospho-borate glasses. Optical analyses of these glasses have been carried out based on the measurement of their absorption, excitation and emission spectra in the visible and NIR region. Apart from analyzing their optical properties, we could also notice a bright orange-red emission (Pr^{3+} glasses) and a bright blue emission (Tm^{3+} glasses) under an UV source. Decay curves of the visible emissions have been plotted to measure lifetimes. From the measured NIR emission spectra of Pr^{3+} and Tm^{3+} doped fluoro-phospho-borate glasses, the NIR emission at 1355 nm of Pr^{3+} glasses and NIR emission at 1809 nm of Tm^{3+}glasses have been observed. Both the series-A&B glasses, with TeO_2 have demonstrated encouraging emission and absorption spectral results. Thus, we could suggest that 69.8 B_2O_3- 10 P_2O_5 - 10TeO_2- 10 AlF_3 of Series-A and 69.8 B_2O_3 - 10 P_2O_5 -10TeO_2 - 10 LiF of Series-B, as two novel optical glasses with as the luminescent ions Pr^{3+} and Tm^{3+} based on NIR emission performance at 1355 nm (Pr^{3+}) and 1809nm (Tm^{3+}) and also based on their visible emission performance for their use in development of solid state lasers and fiber optical amplifiers.

Acknowledgements

This work was supported by the University Grants Commission, Hyderabad in the form of a Minor Research Project sanctioned to one of the authors (BSR) who would like to thank Dr. S. Jelani, Deputy Secretary (UGC-SERO) and also Sri. A. Gangi Reddy, Principal, S.V. Degree College, Kadapa,,India, for their kind support and co-operation in the present study.

References

[1] J. Fernandez, R. Balda, J. L. Adam, J. Phys. C **10,** 4985 (1998).
[2] K. Gatterer, G. Pucker, W. Jantscher, H. P. Fritzer, S. Arafa, J. Non –Cryst. Solids. **231,** 189 (1998).
[3] Agnesi, S. Dell' Acqua, A. Guandalini, G. Reali, F. Cornacchia, A. Toncelli, M. Tonelli, K. Shimamura, T. Fukuda, IEEE, J. Quant. Electron. **37**, 304 (2001).
[4] F. Qu. N. O. Dantas, Phys B. **327**, 79 (2003).
[5] I. M. Batyaev, A. M. Tinus, Opt. Spectrosc. **84,** 584 (1998).
[6] R. Balda, J. Fernandez, A. de Pablos, J. M. Fdez-Navarro, M.A. Arriandiaga, Phys. Rev. B **53** , 5181 (1996).
[7] L. C. Courrol, L. R. P. Kassab, V. D. D. Cacho, S. H. Tatumi, N.U. Wetter, J. Lumin. **102,** 101 (2003).
[8] C. H. Kam, S.Buddhudu, Opt Lasers Eng. **35** , 11 (2001).
[9] G. Wang, J. Opt. Soc. Am. B. **18(2**),173 (2001).
[10] B.V. Mill, A.M. Tkachuk, E.L. Belokoneva, G.I. Ershova, D.I., Miranov, I.K.Razumova, Opt. Spectrosc. **84,** 74 (1998).
[11] Belliveau, T.F& Simkin, D.J, J. Non-Cryst. Solids **110,** 127 (1989).
[12] B.J.Ainslie S.P. Craig, S.T.Davey & B Wakefield, Mater. Lett. **6,** 39 (1988).
[13] J. Dexpert-Ghys, B.Piriou, N. J. Fracillon & C. Sombret, J. Non-Cryst. Solids.**125**, 117 (1990).
[14] J.E.Shelby, L.K.Downie, Phys. Chem. Glasses. **30(4),** 151 (1989).
[15] R. Staske, P.Frobel, M.V.Dirke, S. Mullor, & Barner, K. Solid State Commun. **78,** 647 (1991).
[16] I. Ardelean, M. Toderas, J. Optoelectron. Adv. Mater. **8**(3), 1118 (2006).
[17] R. Ciceo-Lucacel, I. Ardelean, J. Optoelectron. Adv. Mater. **8**(3), 1124 (2006).
[18] C. Tripon, D. Toloman, M. Aluas, C. Filip, I. Ardelean, J. Optoelectron. Adv. Mater. **8**(3), 1129 (2006).
[19] I. Ardelean, V. Timar, J. Optoelectron. Adv. Mater. **9**(4), 840 (2007).
[20] M. Toderas, S. Filip, I. Ardelean, J. Optoelectron. Adv. Mater. **8**(3), 1121 (2006).
[21] I. Ardelean, L. Griguta, J. Optoelectron. Adv. Mater. **9**(7), 2068 (2007).
[22] B. G.Aitken, M. L. Powley, R. M. Morena, B. Z. Hanson, J. Non. Cryst. Solids. **352**, 488 (2006).
[23] W. E. K. Gibbs, D. J. Booth, V. K. Bogdanov, J. Non. Cryst. Solids**. 353,** 1 (2007).
[24] B. Klimesz, G. Dominiak-Dzik, P. Solarz, M. Zelechower, W. Ryba-Romanowski J. Alloy. Comp. **382,** 292 (2004).
[25] B. Klimesz, G. Dominiak-Dzik, P. Solarz, M. Zelechower, W. Ryba-Romanowski J. Alloy. Comp. **403,** 76 (2005).
[26] Anita Rai, Vineet Kumar Rai, Spectrochim. Acta Part. A **63,** 27 (2006).

[27] L. Nagli, O. Gayer, A. Katzir Opt. Mater. **28,** 147 (2006).
[28] A. A. Kaminskii, Laser Crystals, Second Ed., Springer, Berlin (1990).
[29] D. B. Gatch, S. A. Nolmstrom, W. M. Yen, J. Lumin. **83,** 559 (1999).
[30] D. M. Baney, L. Yang, J. Ratcliff, K. W. Chang, Electron. Lett. **31**, 1842 (1999).
[31] K. Wei, D. P. Machewirth, J. Wenzel, E. Snitzer, G. H. Sigel Jr., J. Non. Cryst. Solids. **182,** 257 (1995).
[32] F. Varsanyi, Appl. Phys. Lett.**19,** 169 (1971).
[33] M. Szymanski, J. Karolczak, F. Kacizmarck, J. Appl. Phys. **19**, 27 (1975).
[34] J. Hegarty, D. L. Huber, W. M. Yen, Phys. Rev. B **25,** 5638 (1982).
[35] S. Q. Man, E. Y. B. Pun, P. S. Chung, J. Opt. Soc. Am. B **17,** 23 (2000).
[36] V. V. R. Kanth Kumar, A. K. Bhatnagar, R. Jagannathan, J. Phys. D **34**, 1563 (2001).
[37] P. Babu, C. K. Jayasankar, Physica B. **301,** 326 (2001).
[38] K. K. Mahato, S. B. Rai, D. K. Rai, Phys. Stat. Sol. **174,** 277 (1999).
[39] F. J. Mcaleavey, B. D. Macraith, Electron. Lett. **31,** 1379 (1995).
[40] D. C. Hanna, R. M. Percival, R. G. Smart, Opt. Commun. **75,** 283 (1990).
[41] S. X. Dai, J. H. Yang, S. G. Li, Acta. Opt. Sini. **23,** 105 (2003).
[42] X. Zou, T. Izumitani, J. Non - Cryst. Solids. **162**, 58 (1993).
[43] X. B. Chen, G. Y. Zhange, H. Y. Mao, J. Lumin. **69**, 151 (1996).
[44] A. Brinier, C. Pedrine, B. Morine, Phys. Rev.B. **41,** 5364 (1990).
[45] B. Sudhakar Reddy, S. Buddhudu, Proc. Ind. Nat. Sci. Acad. **73**, 1 (2007).
[46] B. Sudhakar Reddy, S. Buddhudu, Ind. J. Pure & Appl. Phys. **45**, 496 (2007).
[47] K. Binnemans, R. Van Deun, C. Gorller-Walrand, J. L. Adam, J. Non. Cryst. Solids **238**, 11 (1998).
[48] Y. K. Sharma, S. S. L. Surana, C. L. Gehlot, S. P. Tandon, Ind. J. Eng. & Mater. Sci **10**, 215 (2003).
[49] Y. Ohishi, T. Kanamori,T. Kitagawa, S. Takahashi, E. Snitzer, G. H. Sigel Jr., Opt.Lett. **16**, 1747 (1991).
[50] R. Rolli, S. Ronchin, M. Montagna, E. Moser, C. Duverger, V. K. Tikhomirov, A. Jha, M. Ferrari, J. Non -Cryst. Solids **280**, 269 (2001).
[51] C. Duverger – Arfuso, B. Boulard, Y. Jestim, M. Ferrari, A. Chiasera Opt. Mater. **28,** 441 (2006).
[52] A. Sennaroglu, I. Kabalci, A. Kurt, U. Demirbas, G. Ozen, J. Lumin.**116,** 79 (2006).
[53] K. Annapurna, Maumita Das, S.Buddhudu , Physica B. **388,** 174 (2007).
[54] P. Srivastava, S. B. Rai, D. K. Rai, J. Alloy. Comp. **368** (2004).
[55] F. Lohoz, J. M. Almenara, U. R. Rodriguez-Mendoza, I. R. Martin, V. Lavin, J. Appl. Phys. **99,** 053103 (2006).
[56] R. Balda, J. Fernandez, M. A. Arrandiaga, L. M. Lacha, J. M. Fernandez-Navarro, Opt. Mater. **28**, 1253 (2006).

*Corresponding author: sudhakar_b9@rediffmail.com